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EVALUATION OF CERMET MATERIALS SUITABLE FOR LITHIUM-LUBRICATED THRUST BEARINGS FOR HIGH-TEMPERATURE OPERATION

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16. Abstract

Six cermet materials (HfC - 10 wt % W; HfC - 10 wt % TaC - 10 wt % W; HfC - 2 wt % CbC - 8 wt % Mo; HfN - 10 wt % W; HfN - 10 wt % TaN - 10 wt % W; and ZrC - 17 wt % W) were evaluated for possible use as lithium-lubricated bearings in the control system of a nuclear reactor. Tests of compatibility with lithium were made in T-111 (Ta-8W-2Hf) capsules at temperatures up to 1090° C. The tendencies of HfC-TaC-W, HfC-CbC-Mo, and HfN-W to bond to themselves and to the refractory alloys T-111 and TZM when enclosed in lithium-filled capsules under a pressure of 1.4×10^7 N/m^2 (2000 psi) at 980° and 1200° C for 1933 hours were evaluated. Thermal expansion characteristics were determined for the same three materials from room temperature to 1200° C. On the basis of these tests, HfC-10 TaC-10W and HfN-10W were selected as the best and second best candidates, respectively, of the materials tested for the bearing application.

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EVALUATION OF CERMET MATERIALS SUITABLE FOR LITHIUM-LUBRICATED THRUST BEARINGS FOR HIGH-TEMPERATURE OPERATION

by John H. Sinclair and William H. Hendrixson*

Lewis Research Center

SUMMARY

Six refractory cermets (HfC - 10 wt % W; HfC - 10 wt % TaC - 10 wt % W; HfC - 2 wt % CbC - 8 wt % Mo; HfN - 10 wt % W; HfN - 10 wt % TaN - 10 wt % W; and ZrC - 17 wt % W) were evaluated for possible use as lithium-lubricated thrust bearings in the control system of a nuclear reactor. These were evaluated on the basis of lithium compatibility tests, thermal expansion characteristics, and the tendency to bond to samples of the same materials, to each other, and to the candidate control drum shaft materials T-111 and TZM when heated under pressure in lithium. Major emphasis was on the compatibility of the materials with lithium. Tests were performed in tantalum alloy T-111 capsules for 4000 hours at temperature up to 1090° C. Diffusion bonding tests in lithium were made with HfC-10TaC-10W, HfC-2CbC-8Mo, and HfN-10W at temperatures up to 1200° C under a pressure of 1.4×10^7 newtons per square meter (2000 psi) for 1933 hours. Thermal expansion characteristics were determined for these three materials from room temperature to 1200° C.

The HfC-TaC-W and HfC-W were not attacked by lithium in the compatibility tests, but the density achieved with HfC-W was too low for the bearing application. The other four materials showed reaction with lithium to various degrees. The HfC-CbC-Mo, HfN-TaN-W, and ZrC-W materials were eliminated because of lithium compatibility problems, although further fabrication work might lead to more compatible combinations of these materials.

The diffusion bonding test did not uncover any serious problems with the three materials tested. Two of them, HfC-CbC-Mo and HfN-W, showed increasing thermal expansion rates with increasing temperatures.

On the basis of test results, HfC-TaC-W and HfN-W seem to offer the most promise as first and second choices, respectively. But, additional development work and testing are necessary to make a sound choice of a bearing material for the proposed reactor application.

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INTRODUCTION

The NASA-Lewis Research Center has recently terminated work on a technology program for a compact, fast-spectrum nuclear reactor for space electric power generation. The reactor concept is described in reference 1 and is shown in figure 1.

One reactivity control method considered for this reactor involves using movable fuel drums cooled by flowing lithium. This would require thrust bearings to operate in lithium at nominal temperatures of about 950° C. However, 1090° C was selected for compatibility testing because of cooling uncertainties in bearing areas. The design of these bearings is discussed in reference 2, and a sketch is presented in figure 2. Since the technology for this type of bearing was not available, a study was undertaken to evaluate the feasibility of using potential bearing materials in lithium at high temperatures. The specific purpose of this study was to determine the best candidate material for this use, particularly with regard to chemical compatibility and diffusion bonding. Effects of use under dynamic conditions on wear or adequacy of the mechanical properties were not evaluated.

At the outset of this study, six candidate bearing materials were selected by NASA on the basis of previous experience, potential hardness, toughness, high melting points, and thermochemical stability in lithium. The results (ref. 3) of tests on bearing materials for use at lower temperatures showed metal carbides cemented with binder metals to be promising. Refractory metal cemented carbides would have more strength and greater densities than would straight refractory metal carbides (ref. 3). In earlier tests, materials containing tungsten carbide exhibited carbon transfer through potassium to Cb-1Zr capsule walls at 870° C (ref. 4). The otherwise promising material, WC-2 CbC-8Mo, showed transfer of carbon from the WC to a Cb-1Zr capsule wall through lithium at around 600° C (ref. 3). (All bearing material compositions are expressed in wt %.) This carbon transfer occurred because CbC is thermodynamically more stable than WC in a 600° C lithium environment. Titanium carbide and zirconium carbide, however, demonstrated good corrosion resistance in lithium at 815° C (ref. 5). In the bearing materials tested, the thermodynamic system consists of a bonded carbide or nitride candidate bearing material in contact with lithium, which is contained in a T-111 alloy (Ta-8W-2Hf) capsule. A complete and accurate thermodynamic treatment of such a complicated system cannot be carried out with the limited data available. Some indication of the compatibility of the system can, however, be obtained simply from a consideration of the free energy changes involved in a particular reaction in question. For example, it is concluded that the reaction

$$2TaC + 2Li - Li_2C_2 + 2Ta$$

does not occur in the 870° to 1090° C temperature range since the free energy change for the reaction is positive.

The initial selection of the carbides and nitrides for testing was done in part on the basis of their thermochemical stabilities relative to lithium. That is, compounds with the highest negative free energies of formation relative to lithium carbide or lithium nitride were selected for use in the bearing materials. These were HfN, TaN, HfC, ZrC, and TaC. However, although the materials selected are relatively stable in lithium, reactions could still possibly occur. For example, it is well known that the TaC phase has a wide range of homogeneity. In addition, it is possible that carbon has an appreciable solubility in lithium. Thus, carbon could transfer to the lithium by way of a reaction such as

$$TaC + Li \rightarrow Li(xC) + TaC_{1-x}$$

where (xC) represents x moles of carbon dissolved in lithium and TaC_{1-x} is the TaC phase with less than the stoichiometric carbon content. It should be clear, then, that a complete thermodynamic calculation would necessitate knowing the thermodynamic properties as a function of composition.

Another extremely important consideration is the kinetics of the system. The bearing - lithium - T-111 system is inherently an unstable one, and the transport of interstitials (e.g., C or N) in concentration gradients or temperature gradients can be expected until the activity of the interstitial is the same throughout the system. Thus, the observed compatibility behaviors are influenced more by the reaction kinetics than by thermochemical considerations. For example, an unfavorable reaction may proceed slowly enough as to still allow the system to be used in the bearing application. Therefore, actual testing was required to select a bearing material for the reactor application. The six materials (in wt %) tested in this program were the following: HfC-10W, HfC-10TaC-10W, HfC-2CbC-8Mo, HfN-10W, HfN-10TaN-10W, and ZrC-17W.

Note that TiC, another carbide which should be thermodynamically stable in the lithium environment, was not included. It was felt that using a metal foreign to those found in the proposed system (which would use T-111 or Cb-1Zr for tubing) might add further complications to the system. Also, note that the third material listed (HfC-CbC-Mo) is similar to one tested earlier (ref. 3) but with HfC substituted for WC.

Samples of these materials were produced at the Battelle Memorial Institute (under a NASA contract) using existing fabrication technology (ref. 6). These bearing materials were tested in high-temperature/long-term exposures by General Electric under NASA contract. The testing program consisted of three parts:

(1) The six materials were subjected to a chemical compatibility screening test for 000 hours at 870°, 980°, and 1090° C in lithium-filled T-111 (Ta-8W-2Hf) capsules.

(2) Three of the cermet materials were selected (somewhat arbitrarily) for adhesion bonding and thermal expansion tests. These were HfC-TaC-W, HfC-CbC-Mo, and HfN-W. The tendencies of these materials to bond to each other and to candidate control

drum shaft materials (T-111) and TZM) in lithium were determined. Specimens were pressed together at 1.4×10^7 newtons per square meter (2000 psi) for 1933 hours at 980° and 1200° C. The 1200° C temperature was selected to give an accelerated test since bonding of bearings in the control system of a reactor could not be tolerated.

(3) Thermal expansion coefficients were determined from room temperature to 1200° C for the same three materials. The results of the tests at General Electric and the subsequent evaluations at the Lewis Research Center are described in this report.

MATERIALS, APPARATUS, AND PROCEDURE

Materials

The bearing materials used were HfC-10W, HfC-10TaC-10W, HfC-2CbC-8Mo, HfN-10W, HfN-10TaN-10W, and ZrC-17W. It was desired to obtain a continuous metal matrix in all specimens to increase resistance to mechanical shock. The proportions of the constituent materials for the six refractory cermet candidate bearing materials were selected to achieve this goal. Note that 17 weight percent tungsten was used with ZrC but only 10 weight percent tungsten was used with HfN and HfC. This was done to maintain approximately the same atom ratio of tungsten to ceramic material.

The preparation of the bearing material specimens was performed at the Battelle Memorial Institute as described in reference 6. This was done on the basis of existing fabrication technology with very little additional development work. Billets (approximately 7.5 cm in diameter) of the six compositions were prepared by uniaxial hot pressing of blended powders. Two billets were made of each material. Characteristics of the hot-pressed billets are presented in tables I and II. Generally the desired goals of high purity and high density were achieved. However, oxygen levels of the hot-pressed billets were higher than desired; they ranged between 98 and 1300 ppm (table I). A goal of 100 ppm maximum oxygen content had been set, but this could not be achieved without further development work which was beyond the scope of this program. Also, fabrication difficulties were encountered with the HfC-W billets. Thus, the densities of these billets were much lower than those of the others. Rectangular test specimens (0.635 cm by 0.635 cm by 5.08 cm in size) were cut from the billets by grinding and slitting with diamond wheels. The specimens were measured to ±0.0025 centimeter and weighed to ±0.001 gram.

Lithium purified by hot trapping and distillation was used in these tests. A chemical analysis of the lithium for oxygen, nitrogen, and carbon and a spectrographic analysis of other impurities are presented in table III. The T-111 and TZM used in the program were commercially procured to the specifications presented in reference 7.

Testing and Evaluation Procedures

Lithium compatibility testing. - Specimens for determining the compatibility between all six bearing materials and lithium were selected from the rectangular pieces described in the materials section. They were used without further machining for a preliminary 500-hour test made at 980° C for each of the six materials to determine if any of the materials would deteriorate enough to eliminate them from further consideration prior to selection of three candidate materials for diffusion bonding and thermal expansion tests. No damage was observed after this 500-hour test. Hence, it did not aid in the selection of the materials for diffusion bonding or thermal expansion tests. Thus, the 500-hour compatibility test is not discussed further.

Since no changes were observed in the specimens from the 500-hour test, all specimens for the 4000-hour test had one lateral surface polished with 600-grit metallographic paper. This additional surface finishing was done to enhance the detection of small changes that might occur to the bearing surfaces during testing. Prior to testing the bearing material, specimens were ultrasonically cleaned in distilled water and then in ethanol and air dried. They were outgassed for 1 hour at 425° C in a vacuum of 1.3×10^{-3} newton per square meter (10^{-5} torr), the dimensions were measured, and then the specimens were weighed. They were placed in individual T-111 capsules (which had been cleaned as described in ref. 8) within an electron beam welding facility where they were filled with enough lithium to assure coverage of the specimens at test temperature. The capsules then were sealed by electron beam welding. Chemical analyses of lithium samples taken at the beginning and end of the fill were made to check for nitrogen pickup during the fill. The nitrogen pickup was less than 3 ppm. The finished capsules were leak checked with pressurized helium before being subjected to the compatibility test.

Testing was done in a vacuum which varied from 1×10^{-4} newton per square meter (8×10^{-7} torr) at the time the capsules reached the test temperature to 4×10^{-7} newton per square meter (3×10^{-9} torr) at the end of the test. The tests were made at three nominal temperatures: 870°, 980°, and 1090° C. The temperatures were maintained in the ranges of 860° to 882° C, 977° to 982° C, and 1090° to 1100° C for the three test conditions. The capsules were maintained at the desired temperatures for a total of 4000 hours and then furnace cooled. One thermal cycle to room temperature was included in the tests.

After completion of the tests, lithium was vacuum distilled from the specimens in the temperature range of 700° to 750° C for 72 hours at a pressure of 1.3×10^{-3} newton per square meter (10^{-5} torr). The specimens were weighed, then cleaned further in alternate ethanol and water rinses, and finally oven dried with the objective of reaching a constant weight which would indicate removal of all lithium from voids in the bearing materials. The specimens then were measured and prepared for metallographic examination.

Diffusion bonding tests. - A view of the apparatus used for the diffusion bonding tests is presented in figure 3. The bearing materials selected for testing were HfC-TaC-W, HfC-CbC-Mo, and HfN-W. The test capsules were made of T-111. Three test specimen retaining tubes were located in each of the two test capsules. Each tube held six specimens arranged so that each bearing material was tested in contact with itself, with the other two bearing materials, and in contact with the possible shaft materials T-111 and TZM. A series of holes in the walls of the containment tubes allowed access of lithium to the test specimens.

The diffusion bonding specimens were machined from the rectangular cermet test bars or from T-111 or TZM rods into pieces with octagonal cross sections (0.32 cm across the flats). These were cut into 0.635-centimeter lengths. The specimens were stacked in a crisscross fashion in the test capsules as shown in figure 3. Note that a band of tantalum foil (1.3×10^{-2} cm thick) was used to hold the specimens in alinement (fig. 3). The contact areas between abutting specimens was about 0.1 square centimeter. Contact surfaces of bearing test specimens were polished with 600-grit metallographic paper. The test capsules were filled with lithium and sealed by electron beam welding as discussed in the section Lithium compatibility testing. The capsules were heated in a vacuum furnace at a vacuum level of 1.3×10^{-7} newton per square meter. Sufficient weights were added to the pull rod (fig. 3) to produce a pressure of 13.8 meganewtons per square meter (2000 psi). Testing was done for 1933 hours at both $980^{\circ} \pm 10^{\circ}$ C and $1200^{\circ} \pm 10^{\circ}$ C.

After completion of these tests, the specimens were removed, cleaned, and weighed using the procedures described in the section Lithium compatibility testing.

Thermal expansion measurements. - Determinations of the thermal expansion characteristics of the candidate bearing materials HfC-TaC-W, HfC-CbC-Mo, and HfN-W were in an inert gas atmosphere using a resistively heated tungsten tube furnace. Linear expansion measurements were made by sighting paired filar micrometer telescopes on fiducial marks located near the ends of the 5.08-centimeter-long specimen. Detailed descriptions of this apparatus and the procedure used are given in reference 9.

Metallographic examination. - Specimens from the lithium-compatibility and diffusion-bonding tests were metallographically examined using standard mounting and polishing techniques. For the bearing cermets, the etchant used was a mixture of 50 cubic centimeters of lactic acid, 25 cubic centimeters of nitric acid, 5 cubic centimeters of hydrofluoric acid, and 20 cubic centimeters of distilled water. For T-111, the etchant was 30 grams ammonium bifluoride ($NH_4F \cdot HF$), 50 cubic centimeters of nitric acid, and 20 cubic centimeters of distilled water. For TZM, the etchant was Murikami's solution (10 g $K_3Fe(CN)_6$ + 10 g KOH + 100 cm^3 distilled water).

RESULTS AND DISCUSSION

Compatibility Testing in Lithium

Six potential materials for lithium-lubricated thrust bearings were tested for compatibility with lithium for 4000 hours at 870° C, 980° C, and 1090° C. These bearing materials were enclosed in lithium-filled T-111 capsules. The results of the posttest evaluation of these specimens are included in tables IV to VI and figures 4 to 9.

There were some weight changes found in the bearing material specimens following the 4000-hour lithium compatibility tests (table IV). The HfC-W specimens showed an average weight loss per specimen of around 140 milligrams or about 10 milligrams per square centimeter of surface area. One of the specimens had lost material by chipping - either during the test or during posttest cleaning. The HfC-W lost much more weight than the other five materials. This is attributed to the porous, low-density structure obtained during fabrication of HfC-W. This difference in density is apparent when comparing the photomicrographs of the unexposed specimens (figs. 4(a), 5(a), 6(a), 7(a), 8(a), and 9(a)). The HfC-W (fig. 4(a)) has many more unconsolidated particles than the other five materials. The primary cause of the large weight loss of this material is believed to be loss of some of this unconsolidated material, either during testing or during the cleaning of the specimens following the tests. The HfC-TaC-W and ZrC-W specimens showed small weight losses; five of the six specimens showed evidences of chipping. The other three materials showed a tendency to gain weight. The specimens averaged about a 6-milligram increase in weight. This may be attributed to incomplete lithium removal during posttest cleaning or possibly to surface film formations which occurred during testing.

Figure 7(d) shows HfN-W tested at 1090° C. Something happened at the surface of this specimen that caused it to etch differently than the rest of the specimen. This specimen showed the greatest weight gain of any of the specimens tested (15.3 mg). Alterations of a bearing surface during operation in lithium could have an effect on bearing life and surface characteristics. In general, weight changes found in any of the specimens cannot be strictly attributed to a specific cause such as lithium attack, lithium retention, chipping, or surface film formation.

Dimensional changes of the six materials as a result of exposure to lithium for 4000 hours at the three temperatures are presented in table V. In general, most changes are very small. The largest percentage change noted for any of the 54 dimensional checks was an increase of 0.28 percent in one of the width determinations on the HfN-TaN-W specimen exposed at 1090° C. Both this material and the other nitride composition, HfN-W, exhibited a trend of dimensional growth with increasing exposure temperature.

As discussed in the Testing and Evaluation Procedures section, one surface of each bearing material was polished with 600-grit paper. These are the surfaces shown in figures 4 to 9 which compare the microstructures of the untested bearing materials with those tested at the three test temperatures. Note that the goal of obtaining a continuous metal matrix was not achieved in all cases.

Figure 4 presents the microstructures of HfC-W. A comparison of figure 4(a) (untested material) with figures 4(b), (c), and (d) indicates that HfC-W is compatible with lithium at all the temperatures tested. But the material could not be produced in a form with sufficient density to be considered as a serious candidate for bearing applications. It was by far the most porous of the six materials tested. Further fabrication development to obtain fully dense material was beyond the scope of this work.

Figure 5 presents the microstructures of HfC-TaC-W before and after the 4000-hour lithium compatibility test. All surfaces appeared to be unattacked. This material appears to be the best bearing choice from the viewpoint of compatibility with lithium.

The HfC-CbC-Mo showed evidence of attack in lithium (fig. 6). Although attack appears to be slight and to occur only at 980° C or above, examination of the specimen tested at 1090° C at a higher magnification (X1000) than that shown in figure 6(d) revealed grain boundary attack to a depth of 2.75×10^{-3} centimeter along the surface exposed to lithium, and large areas of the bearing material surface tended to spall off. Hence, this material was judged to be unsuitable for the proposed bearing application.

Figure 7 presents the microstructures of HfN-W. A comparison of figure 7(a) (untested material) with 7(b) reveals that there was no visible attack of the bearing material surface by lithium at 870° C. But the material tested at 980° C had a band 4×10^{-4} centimeter deep (fig. 7(c)) that etched differently than the matrix. This possibly indicates a depletion or contamination zone. For the specimen tested at 1090° C (fig. 7(d)), this zone is 1.4×10^{-3} centimeter deep. Nevertheless, the bearing surface of these specimens remained smooth. These zones do not appear to be epitaxial growths or films deposited on the original bearing surface that might contribute to the increase in weight observed, but rather zones that have reacted with lithium in some manner. The tendency of HfN-W to chip was observed during evaluation of the test results, and this might cause a problem in an actual bearing application.

As illustrated in figure 8, HfN-TaN-W showed little, if any, attack at 870° C but it was attacked to a depth of 3×10^{-3} centimeter at 980° C and 4×10^{-3} centimeter at 1090° C. This material appears to be unsuitable for bearing application on the basis of the lithium attack observed (fig. 8(d)).

First traces of attack of ZrC-W due to exposure to lithium may be observed in figure 9(b), the photomicrograph of the 870° C test. At 980° C the attack was not continuous along the specimen surface (fig. 9(c)) but penetrated to a depth of 1.6×10^{-3} centimeter. Maximum attack depth remained about the same at 1090° C, but there was

continuous attack along the bearing material surface (fig. 9(d)). Hence, the material is considered unsuitable for the reactor bearing application.

A summary of results from the lithium compatibility tests is presented in table VI. Both HfC-W and HfC-TaC-W appear completely compatible with lithium at all test temperatures, but dense HfC-W was not achieved. This might be achieved if more fabrication development work were done. HfC-CbC-Mo seems to be compatible at 870° C but not at 980° or 1090° C. The HfN-W seems excellent at 870° C and the surface remains smooth at 980° and 1090° C in spite of some surface reactions. Whether the reacted surfaces would still act as good bearing surfaces would have to be determined by additional testing. Both HfN-TaN-W and ZrC-W seem compatible at 870° C, but they are too seriously attacked at the higher temperatures to be considered useful as bearings for the reactor application that prompted this study.

Diffusion Bonding

Three of the bearing materials (HfN-W, HfC-TaC-W, and HfC-CbC-Mo) were selected as having the most probable chance for success for diffusion bonding tests. The purpose was to determine the tendency of these materials to bond to specimens of the same material, to each other, and to the candidate control drum shaft materials T-111 and TZM with the test specimens being surrounded with lithium.

In a reactor the bearings surfaces would be moved with respect to each other only occasionally with long periods of immobility. Any tendency of the bearing surfaces to stick together could not be tolerated. Any bonding of the bearing surfaces in a reactor would increase the torque required to activate the fuel drums. Bearings would be damaged if any bearing material were pulled out of a bearing surface when the bonds were broken on fuel drum rotation. It was determined by contact area calculations that the maximum pressure that the bearings in a reactor might be subjected to would be around 1.4×10^7 newtons per square meter (2000 psi). Specimens were pressed together at this pressure for 1933 hours at 980° and 1200° C.

The results of the diffusion bonding tests are presented in table VI, which also presents a summary of the lithium compatibility tests. None of the bearing materials bonded to themselves or to each other at either test temperature. However, bonding was observed between some of the bearing materials and the candidate shaft materials.

The best material for use in an application requiring a cermet to move against a metal would be HfC-TaC-W. This material did not bond to either TZM or T-111 at 980° C nor to T-111 at 1200° C. However, it did bond slightly to TZM at 1200° C. A few particles of cermet pulled out and stuck to the TZM when the bonded couple was separated after testing. The HfN-W appears to be usable against either alloy at 980° C, but

it bonded to both alloys at 1200° C. The HfC-CbC-Mo bonded to T-111 (but not to TZM) at 980° C and to both T-111 and TZM at 1200° C.

Photomicrographs of typical cermet-metal bonds are shown in figure 10. Figure 10(a) shows the HfC-CbC-Mo interface with TZM, and figure 10(b) shows the interface between HfN-W and T-111. Note also in figure 10(a) that TZM was distorted by the pressure applied at high temperature to the couples. Figure 11 illustrates the effect of test temperature on the tendency of HfC-CbC-Mo to bond to TZM. No bonding occurred at 980° C (fig. 11(a)), but the cermet stuck to the metal at 1200° C (fig. 11(b)). Note that the cermet surface damage is not limited to the area that contacted TZM (at the center of the specimen). Figure 12 shows a specimen of this cermet that was tested in contact with T-111 at 980° C. The surface that contacted T-111 pulled off from the specimen in the same manner as that shown in figure 11(b), but one of the specimen surfaces that was not in contact with another specimen spalled off. Therefore, this material was judged to be unsuitable for the proposed bearing application.

Thermal Expansion

The thermal expansion coefficients of the three candidate bearing materials HfC-TaC-W, HfC-CbC-Mo, and HfN-W were measured from room temperature to 1200° C using the thermal expansion apparatus described in reference 9. Two separate runs were made on each of the specimens. Thermal expansion data for the three specimens, along with the least square fit of the data, are shown in figure 13. The data were fit to the quadratic expression

$$\frac{L_T - L_{25}}{L_{25}} 100 = A_0 + A_1 T + A_2 T^2 \qquad (1)$$

in which L_T is the measured length at a specified elevated temperature T (in °C), L_{25} the length at room temperature (i.e., 25° C), and A_0, A_1, and A_2 the empirically determined constants. The data for HfC-TaC-W did not show significant departure from linearity over the temperature range measured; that is, $A_2 = 0$ for this material. For the other two specimens, A_2 was significant, giving the normal upward curvature of the plot of percent linear expansion as a function of temperature. This indicates that the expansion coefficient increased with temperature.

The relative standard (rms) deviation ranged from ±2.5 percent for the HfC-CbC-Mo measurements to ±6.9 percent for the measurements on HfN-W. This precision is considered good in view of the fact that the maximum length change measured was only 0.36 millimeter.

Table VII gives the least square constants for each of the materials for percent linear expansion (eq. (1)). From the expression for percent linear expansion, one can derive the constants to give the mean coefficient of thermal expansion as a function of temperature. The mean coefficient of linear expansion α_m between the reference temperature T_{25} and some temperature T is defined as

$$\alpha_m = \frac{L_T - L_{25}}{L_{25}(T - T_{25})} = B_0 + B_1 T \tag{2}$$

where the equation, which is linear in temperature, results from the percent linear expansion expression which is quadratic in temperature. The symbols used in this equation are the same as in equation (1), and B_0 and B_1 are empirically determined constants. Least square constants for the mean thermal expansion coefficients for the three materials are given in table VIII.

Applicability of Results

The compatibility results in general agree with the theoretical considerations that were used in selection of the candidate bearing materials. The bearing material specimens did not lose much weight during the 4000-hour lithium exposure tests (except for HfC-W which could be explained by loss of unconsolidated particles).

Two of the materials, HfC-W and HfC-TaC-W, showed no attack by lithium. These materials behaved as would be expected on the basis of selection. The other four showed varying amounts of attack, but the reasons for attack cannot be assigned to a specific single cause. In addition to losses due to unconsolidated particle weight, losses or surface attack might be related to factors such as reaction kinetics or specimen oxygen level.

Little is known about the effect of oxygen in the cermets on their corrosion resistance in lithium. But high oxygen contents should be gettered by lithium (because of the great stability of Li_2O) which could lead to intergranular penetration by lithium and deterioration of the bearing materials. This may be the cause of some of the attack observed in this study. A maximum goal of 100 ppm was set for the oxygen content of the bearing materials, but this was not achieved (table I). If additional time and money had been spent on improving bearing material fabrication techniques, reductions in the oxygen levels of bearing materials could probably have been achieved. Thus, some of the materials that exhibited lithium attack may be improved by lowering the oxygen content. The oxygen content in the lithium was also kept low to avoid the possibility of formation

of complex oxides with the bearing materials which are thermodynamically more stable at around 1200° C than the carbides or nitrides.

Since neither the posttest lithium nor the containment material (T-111) from the compatibility tests were analyzed chemically (for economic reasons), the amount of solutioning or any mass transfer to the walls of the containment material are not known. But because weight losses of the bearing specimens were very small, it may be assumed that very little if any of either phenomena occurred.

Some of the bearing materials (HfC-CbC-Mo, HfN-TaN-W, and HfN-W) generally showed slight weight gains during the compatibility tests. These gains were attributed to lithium retention, surface film formations, or both. If films formed on the bearing surfaces, these films (or removal of the same during bearing movements) might affect the frictional characteristics or surface characteristics of the bearings. Further testing would be required to determine if this would be a problem.

On the bases of the tests run, none of the bearing materials can be positively ruled out of further consideration for bearing use because (1) further development work might lead to more satisfactory materials ratios, or (2) new fabrication procedures might result in satisfactory bearings. However, of the actual specimens tested, HfC-TaC-W appears to be the best choice. In any further effort of this type it would be wise to concentrate on studying HfC-TaC-W or possibly improving fabrication procedures for HfC-W in order to obtain high density bearing specimens since this material was also unaffected by the lithium compatibility testing. The HfN-W seems to be the second best choice: it still has a smooth surface, even though there has been some change at the bearing surface due to the 4000-hour lithium compatibility testing.

The thermal expansion information was necessary not so much to aid in selecting a bearing material but to enable designers to allow for the differences between expansion characteristics of the bearing materials and the other structural materials used in conjunction with it. The increasing expansion coefficients with increasing temperatures found with HfC-CbC-Mo and HfN-W are significant in that larger clearances would be required than if the expansion coefficients were constant.

Recommendations for Further Work

More work would have to be done to definitely select a bearing material for use in high-temperature lithium-cooled reactors. But based on the results of this study, it is recommended that future studies concentrate on improvement of HfC-TaC-W or on achieving higher density HfC-W material since these were the most compatible in the 4000-hour lithium compatibility test. Further development of these cermets appears warranted. Since no development work was done prior to fabrication of the bearing material billets, fabrication procedures could undoubtedly be improved. Proportions of the

materials present may not represent the optimum formulation for the bearing application. The oxygen content of the bearing materials should be reduced, and this could be done with further development work. The present ratios of major constituents in each of the materials may not necessarily give bearings with optimum frictional characteristics. This would have to be studied. Also, corrosion loop tests or other dynamic testing should be done to look for thermal gradient mass transfer under more severe conditions. Effects of long dwell times on mating bearing parts also should be studied. And finally, effects of irradiation on the bearing life and performance need to be determined.

CONCLUSIONS

Six refractory cermets (HfC - 10 wt % W, HfC - 10 wt % TaC - 10 wt % W, HfC - 2 wt % CbC - 8 wt % Mo, HfN - 10 wt % W, HfN - 10 wt % TaN - 10 wt % W, and ZrC - 17 wt % W) were evaluated for possible use as lithium-lubricated bearings in a control system of a nuclear reactor. The evaluation was primarily based on lithium compatibility tests at temperatures to 1090° C and tests of the tendency of the cermets to bond to themselves and to each other when heated under pressure in lithium at temperatures to 1200° C. Based on this study, it is concluded that HfC-10TaC-10W is the most suitable bearing material of those tested for service in lithium. The HfN-10W is the second choice, but this material appears to have low resistance to chipping and does show some reactions with lithium. This conclusion is based on the following principal results:

1. In a compatibility test in lithium for 4000 hours at temperatures up to 1090° C, HfC-10TaC-W and HfC-10W exhibited no indications of lithium attack. (But the latter material was eliminated from further consideration because the fabrication technology for this material is not adequate to achieve high density.) The other four materials showed reactions in the lithium to depths of from 1.4×10^{-3} to 4×10^{-3} centimeter.

2. Tests to determine the tendency of three of the materials to bond to themselves, to each other, or to T-111 or TZM when pressed together in lithium at 1.4×10^{7} newtons per square meter (2000 psi) at 980° or 1200° C showed that HfC-10TaC-10W and HfN-10W were both acceptable. However, HfC-2CbC-8Mo lost large areas of specimen surface due to spalling.

3. The thermal expansion coefficient for HfC-TaC-W was linear with increasing temperature, but it increased with temperature for HfC-CbC-Mo and HfN-W. Allowances for this would have to be made in design work using any of these materials.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 18, 1974,
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TABLE I. - CHEMICAL ANALYSIS OF HOT-PRESSED BILLETS

Material	Billet designation	Amount of indicated element found in billet, wt %									
		Hf	Zr	Ta	W	Nb	Mo	C	C_{free}	N_2	O_2
HfC-10W	A	85.1	-----	----	9.67	----	----	5.48	<0.01	----	0.0440
	B	85.0	-----	----	9.58	----	----	5.42	<.01	----	.0500
HfC-10TaC-10W	A	74.7	-----	9.20	10.00	----	----	5.88	<0.01	----	0.0330
	B	74.0	-----	9.33	10.20	----	----	5.93	<.01	----	.0470
HfC-2CbC-8Mo	A	83.5	-----	----	-----	1.82	8.37	6.27	<0.01	----	0.0470
	B	84.4	-----	----	-----	1.82	8.47	6.30	<.01	----	.0270
HfN-10W	A	83.5	-----	----	10.20	----	----	----	-----	4.25	0.0320
	B	82.4	-----	----	9.70	----	----	----	-----	2.66	.0025
											[a].0490
HfN-10TaN-10W	A	77.0	-----	9.48	9.55	----	----	----	-----	2.90	0.0130
	B	77.3	-----	9.60	9.52	----	----	----	-----	5.94	.0098
ZrC-17W	A	----	73.70	----	16.33	----	----	8.30	<0.01	----	0.1300
	B	----	73.74	----	16.30	----	----	8.24	<.01	----	.0650

[a]Reanalyzed.

TABLE II. - DENSITY AND GRAIN SIZE OF HOT-PRESSED BILLETS

Material	Billet	Theoretical density,[a] g/cm^3	Average bulk density[b]		Metallographic density,[c] percent of theoretical	Maximum grain size, cm
			g/cm^3	Percent of theoretical		
HfC-10W	A	13.025	10.44	80.1	65.0	1.3×10^{-3}
	B		10.76	82.6	72.5	1.3×10^{-3}
HfC-10TaC-10W	A	13.231	11.88	89.8	91.3	1.1×10^{-3}
	B		11.86	89.7	89.3	7.6×10^{-4}
HfC-8Mo-2CbC	A	12.223	11.10	90.8	91.2	7.6×10^{-4}
	B		11.16	91.3	91.0	5.1×10^{-4}
HfN-10W	A	14.210	13.38	94.1	97.9	1.8×10^{-3}
	B		13.41	94.3	98.2	2.0×10^{-3}
HfN-10TaN-10W	A	14.249	13.85	96.9	99.3	1.8×10^{-3}
	B		13.85	96.9	99.4	1.8×10^{-3}
ZrC-17W	A	7.420	7.32	98.7	87.1	5.1×10^{-4}
	B		7.36	99.1	91.6	5.1×10^{-4}

[a]Calculated for the nominal composition.

[b]Calculated from specimen weight and measurements.

[c]Measured by point-count technique.

TABLE III. - LITHIUM ANALYSIS

[ppm by weight for all elements. All elements except oxygen, nitrogen, and carbon determined by emission spectroscopy.]

Oxygen	28	Iron	5
Nitrogen	2,3	Magnesium	5
Carbon	76	Manganese	<5
Silver	<5	Molybdenum	<5
Aluminum	5	Sodium	---
Boron	<75	Nickel	<5
Barium	<50	Lead	<50
Beryllium	<5	Silicon	<5
Calcium	25	Tin	<25
Columbium	<25	Strontium	50
Cobalt	<5	Titanium	<25
Chromium	<5	Vanadium	<25
Copper	5	Zirconium	<25

TABLE IV. - WEIGHT CHANGE DATA FOR 4000-HOUR EXPOSURE

OF BEARING TEST SPECIMENS IN LITHIUM

Material	Test temperature, °C	Pretest weight, g	Weight change		Remarks
			mg	mg/cm^2	
HfC-10W	870	20.1190	-169.0	-12.32	
	980	20.7024	-123.8	-8.96	
	1090	20.7687	-132.9	9.68	Chipping of specimen corners observed[a]
HfC-10TaC-10W	870	24.0987	-21.3	-1.56	Chipping of specimen corners observed
	980	24.0595	-51.0	-3.72	Chipping of specimen corners observed
	1090	24.1462	-20.1	-1.47	Chipping of specimen corners observed
HfC-2CbC-8Mo	870	22.6099	6.0	0.44	Chipping of specimen corners observed
	980	23.0097	14.3	1.04	
	1090	22.8699	4.7	.34	
HfN-10W	870	27.5597	1.7	0.12	
	980	27.4314	-1.8	-.13	Chipping of specimen corners observed
	1090	27.2861	15.3	1.12	
HfN-10TaN-10W	870	28.1642	-1.8	-0.13	
	980	28.2559	1.1	.08	
	1090	28.2700	3.0	.22	Chipping of specimen corners observed
ZrC-17W	870	14.2956	-5.4	-0.39	Chipping of specimen corners observed
	980	14.3489	-8.1	-.81	Chipping of specimen corners observed
	1090	14.2834	-2.1	-.15	

[a]For all cases, chipping may have occurred during testing or during posttest cleaning.

TABLE V. - DIMENSIONAL CHANGES OF BEARING MATERIALS SPECIMENS AS RESULT OF EXPOSURE TO LITHIUM FOR 4000 HOURS AT VARIOUS TEMPERATURES

Bearing materials	Test temperature, °C	Dimensional changes, percent of original dimension (a)		
		Length	Width 1	Width 2
HfC-10W	870	-0.025	0.04	-0.04
	980	.035	-.08	[b]0
	1090	.050	-.04	.04
HfC-10TaC-10W	870	0	-0.08	-0.04
	980	.010	-.04	-.04
	1090	-.010	-.04	-.04
HfC-2CbC-8Mo	870	-0.025	0	-0.04
	980	-.010	0	0
	1090	-.15	-.04	-.04
HfN-10W	870	0	0	0
	980	.025	.04	0
	1090	.035	.20	.12
HfN-10TaN-10W	870	0	0	-0.04
	980	.010	0	-.04
	1090	.065	.28	.08
ZrC-17W	870	0	-0.04	0
	980	-.005	0	-.08
	1090	0	0	-.08

[a]Length, 5.08 cm; width 1, 0.635 cm; width 2, 0.635 cm.
[b]0 means < 0.05 percent change in length or width.

TABLE VI. - SUMMARY OF LITHIUM COMPATIBILITY AND DIFFUSION BONDING TESTS

Material	Test temperature, °C	Lithium compatibility, 4000-hr test		Diffusion bonding test in lithium, 1933 hours, 1.4×10^{7} N/m^2 (2000 psi)
		Maximum depth of lithium attack, cm	Remarks	
HfC-10W	870	None observed	Compatible, but eliminated because of low density	NT[a]
	980	None observed	Compatible	NT
	1090	Microscopically thin surface film observed	Compatible	NT
HfC-10TaC-10W	870	None observed	Compatible	NT
	980	None observed	Compatible	Did not bond to itself, HfC-CbC-Mo, HfN-W, TZM, or T-111
	1090	None observed	Compatible	NT
	1200	NT	NT	Did not bond to itself, HfC-CbC-Mo, HfN-W, or T-111; very slight bond to TZM
HfC-2CbC-8Mo	870	None observed	Compatible	NT
	980	2.5×10^{-3}	Intergranular attack; incompatible	Did not bond to itself, HfC-TaC-W, HfN-W, or TZM; bonded to T-111
	1090	2.8×10^{-3}	Intergranular attack; incompatible	NT
	1200	NT	NT	Did not bond to itself, HfC-TaC-W, or HfN-W; bonded to TZM and T-111
HfN-10W	870	Microscopically thin surface film observed	Surface smooth; compatible	NT
	980	4.0×10^{-4}	Band of depletion or comtamination; surface smooth	Did not bond to itself, HfC-TaC-W, HfC-CbC-Mo, TZM, or T-111
	1090	1.4×10^{-3}	Band of depletion or contamination; surface smooth	NT
	1200	NT	NT	Did not bond to itself, HfC-TaC-W, or HfC-CbC-Mo; bonded to TZM and T-111
HfN-10TaN-10W	870	Microscopically thin surface film observed	Film not continuous, compatible	NT
	980	3.0×10^{-3}	Continuous film plus intergranular attack; incompatible	
	1090	4.0×10^{-3}	Continuous film plus intergranular attack; incompatible	
ZrC-17W	870	Thinnest observable trace	Compatible	NT
	980	1.6×10^{-3}	Intergranular, noncontinuous attack; incompatible	
	1090	1.6×10^{-3}	Continuous attack along surface; incompatible	

[a]Not tested, NT.

TABLE VII. - LEAST SQUARE CONSTANTS FOR PERCENT LINEAR EXPANSION EQUATION

$$\frac{L_T - L_{25}}{L_{25}} 100 = A_0 + A_1 T + A_2 T^2$$

[Temperature range, 25° to 1200° C.]

Material	Constants		
	A_0	A_1	A_2
HfC-10TaC-10W	-0.015	5.855×10^{-4}	0
HfC-2CbC-8Mo	-.014	5.660×10^{-4}	4.02×10^{-8}
HfN-10W	-.015	6.095×10^{-4}	7.03×10^{-8}

TABLE VIII. - LEAST SQUARE CONSTANTS FOR MEAN THERMAL EXPANSION COEFFICIENTS

$$\alpha_m = \frac{L_T - L_{25}}{L_{25}(T - 25)} = B_0 + B_1 T, \ ^{\circ}C^{-1}$$

[Temperature range, 25° to 1200° C.]

Materials	Constants	
	B_0	B_1
HfC-10TaC-10W	5.855×10^{-6}	0
HfC-2CbC-8Mo	5.670×10^{-6}	4.02×10^{-10}
HfN-10W	6.113×10^{-6}	7.03×10^{-10}

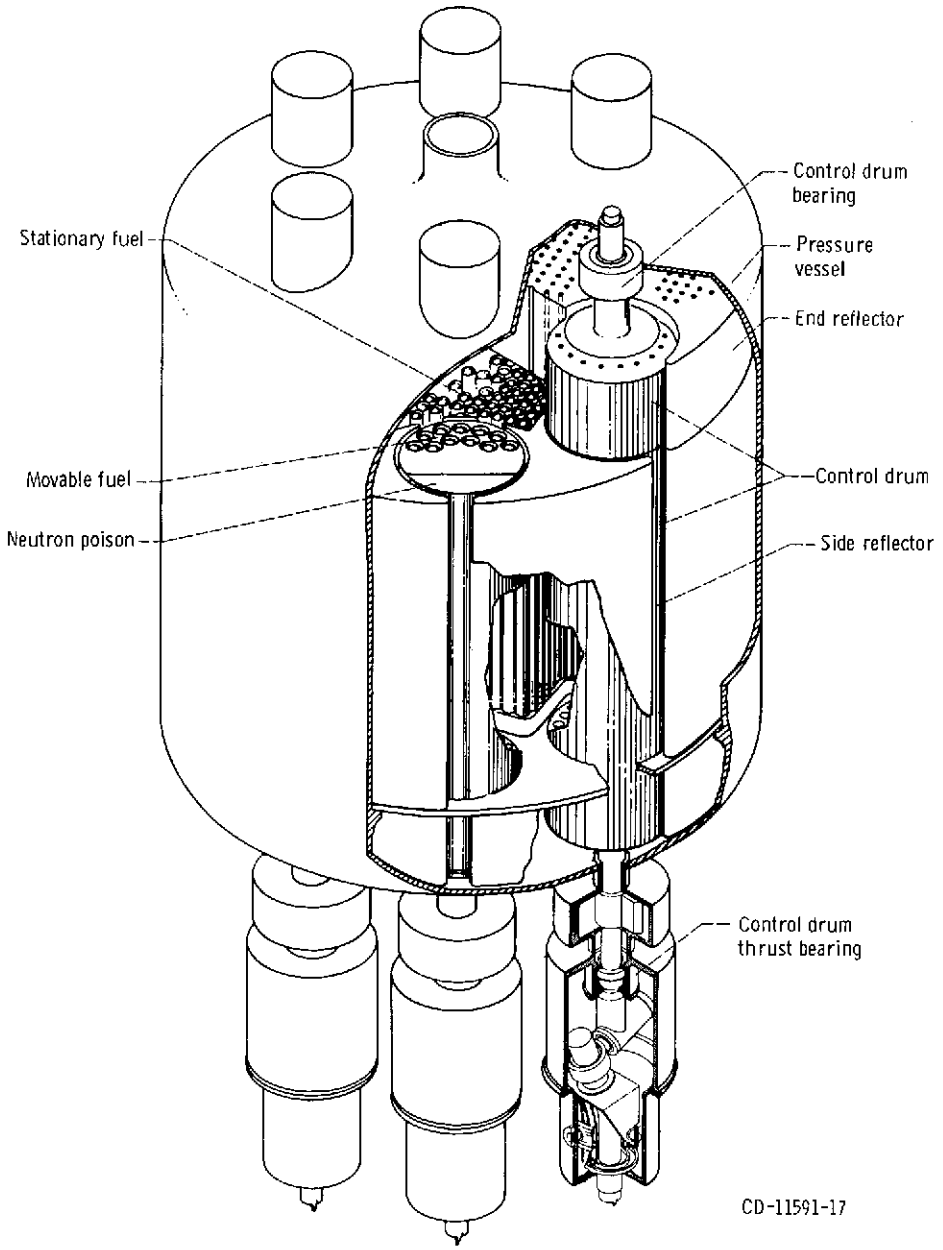


Figure 1. - Compact fast reactor, reference conceptual design.

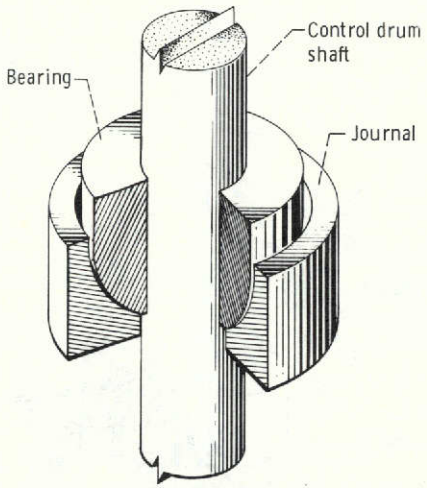


Figure 2. - Combined journal and thrust bearing.

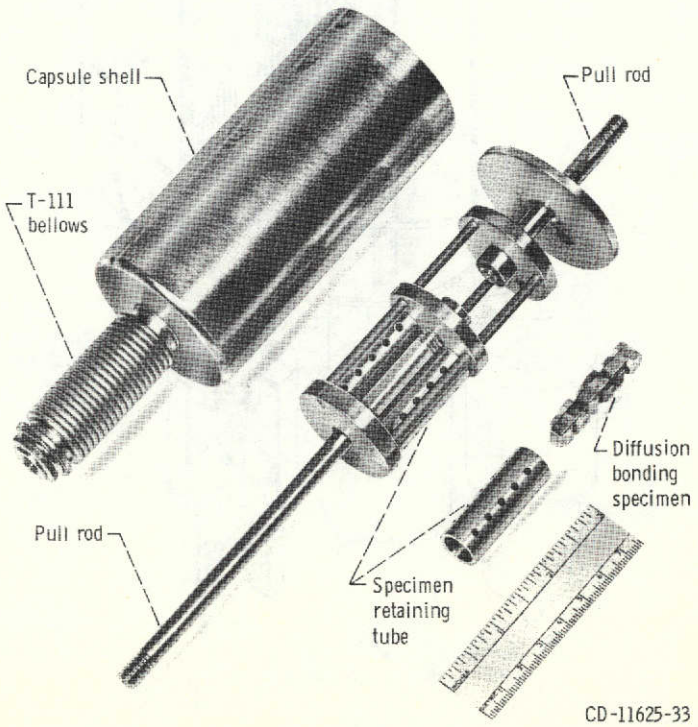
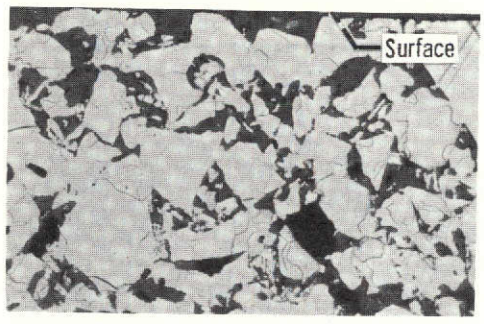
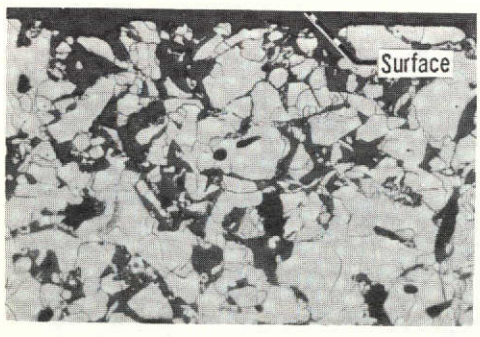


Figure 3. - T-111 diffusion bonding capsule.

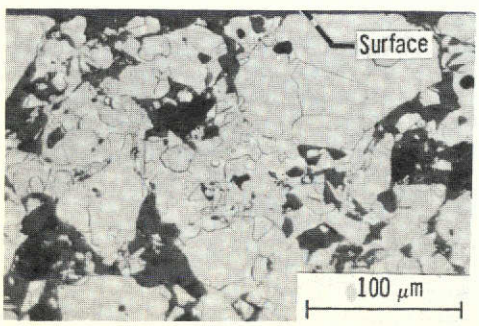
(a) Before exposure to lithium.



(b) Exposed to lithium at 870° C.



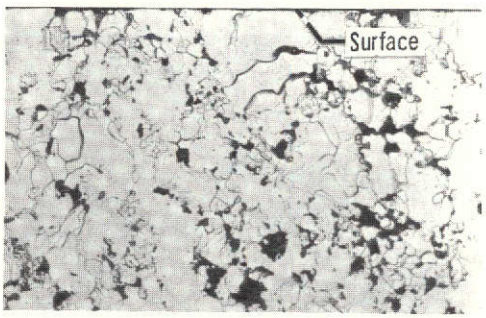
(c) Exposed to lithium at 980° C.



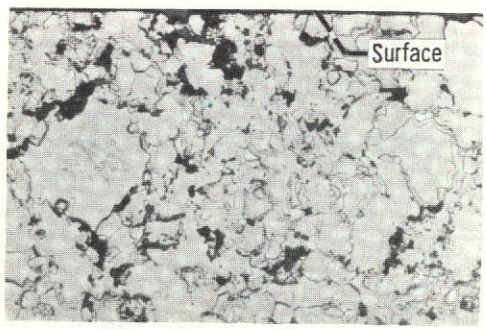
(d) Exposed to lithium at 1090° C.

Figure 4. - Microstructures of surface regions of HfC-10W specimens before and after exposure to lithium for 4000 hours. Etched.

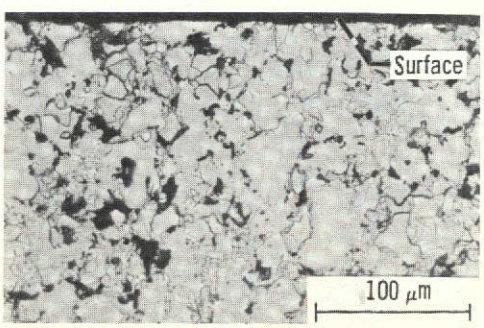
(a) Before exposure to lithium.



(b) Exposed to lithium at 870° C.

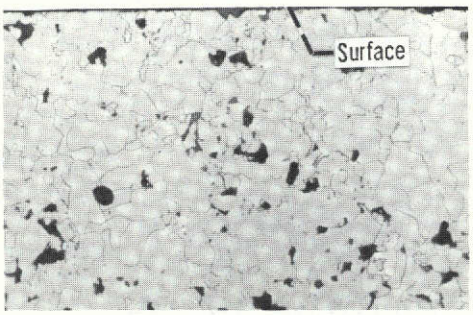


(c) Exposed to lithium at 980° C.

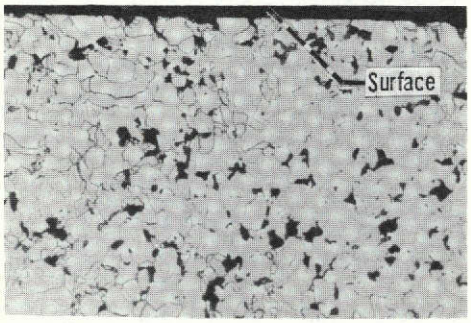


(d) Exposed to lithium at 1090° C.

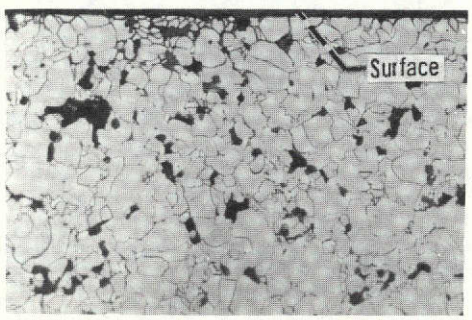
Figure 5. - Microstructures of surface regions of HfC-10TaC-10W specimens before and after exposure to lithium for 4000 hours. Etched.



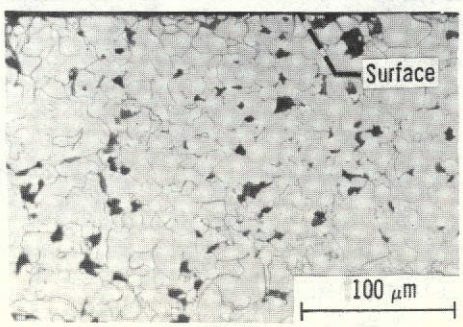
(a) Before exposure to lithium.



(b) Exposed to lithium at 870° C.

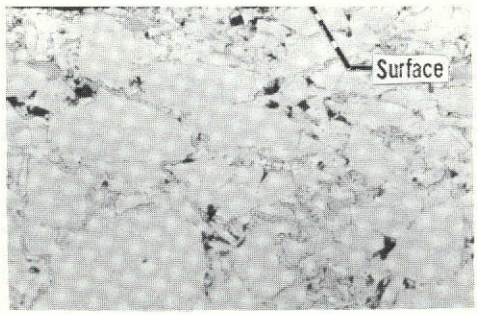


(c) Exposed to lithium at 980° C.

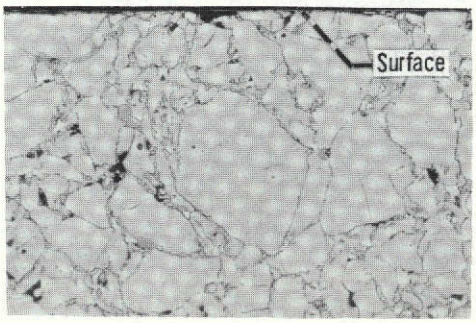


(d) Exposed to lithium at 1090° C.

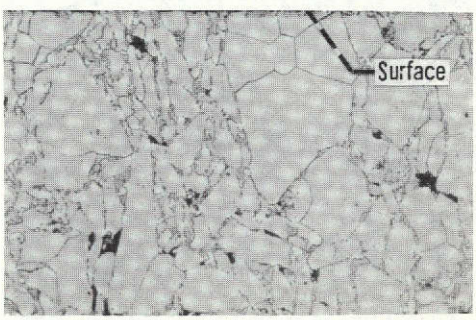
Figure 6. - Microstructures of surface regions HfC-2CbC-8Mo specimens before and after exposure to lithium for 4000 hours. Etched.



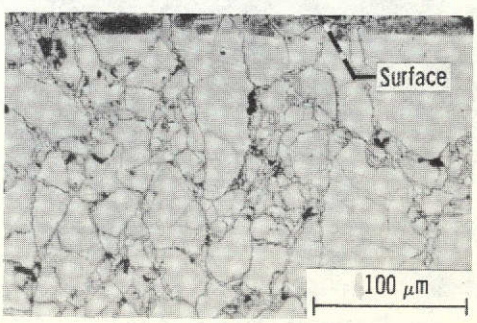
(a) Before exposure to lithium



(b) Exposed to lithium at 870° C.

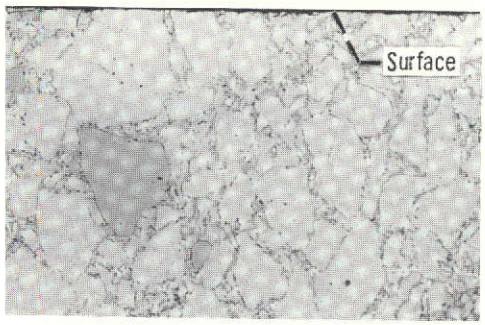


(c) Exposed to lithium at 980° C.

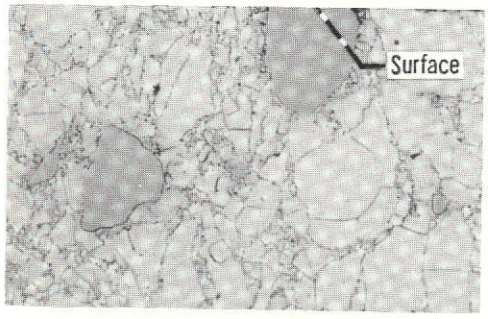


(d) Exposed to lithium at 1090° C.

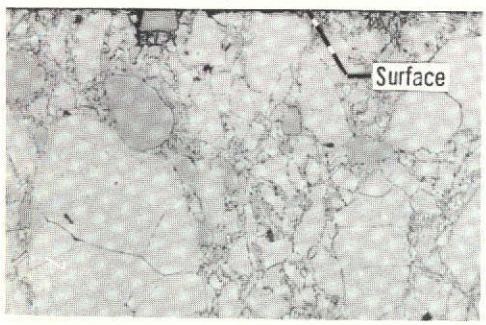
Figure 7. - Microstructures of surface regions of HfN-10W specimens before and after exposure to lithium for 4000 hours. Etched.



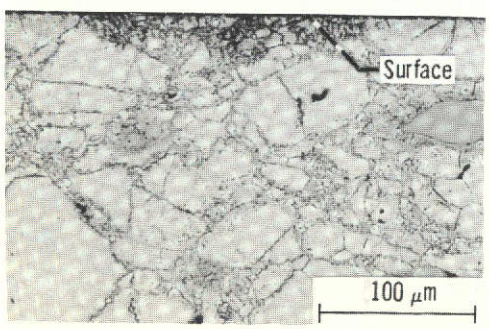
(a) Before exposure to lithium.



(b) Exposed to lithium at 870° C.



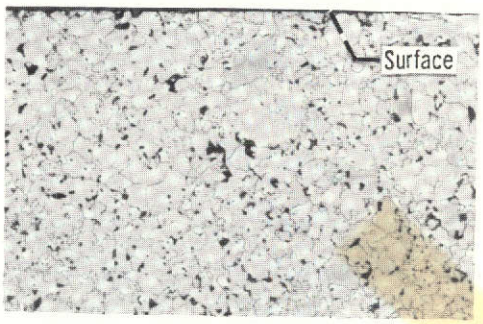
(c) Exposed to lithium at 980° C



(d) Exposed to lithium at 1090° C.

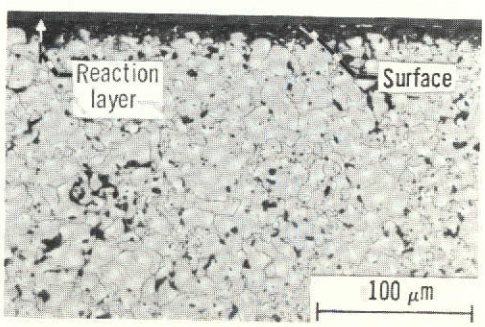
Figure 8. - Microstructures of surface regions of HfN-10TaN-10W specimens before and after exposure to lithium for 4000 hours. Etched.

(a) Before exposure to lithium.



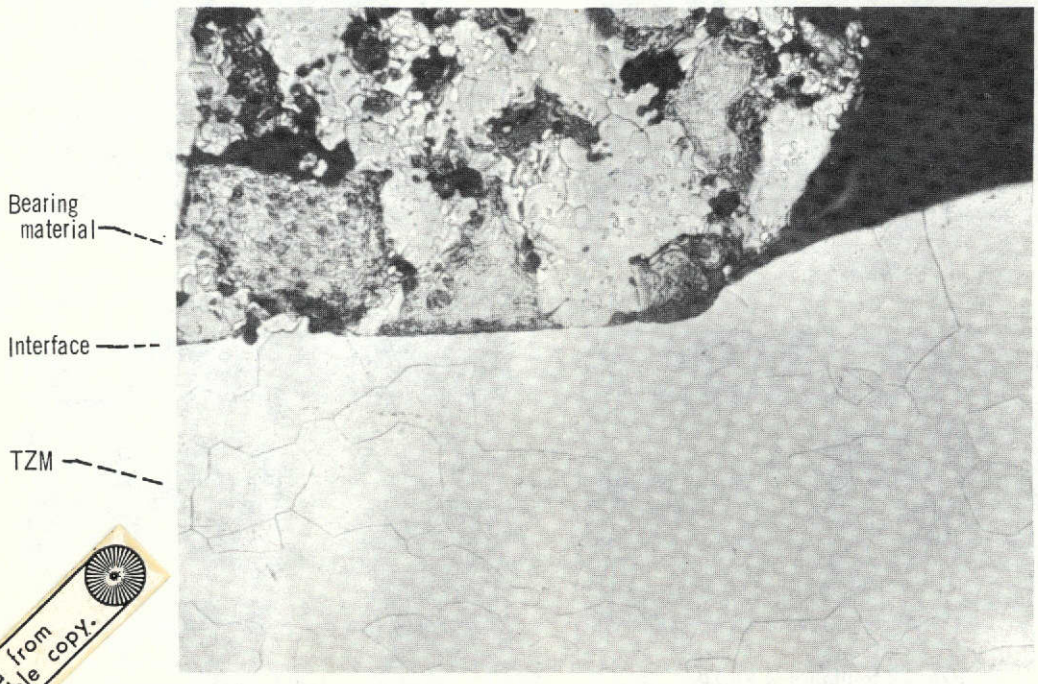
(b) Exposed to lithium at 870° C.

(c) Exposed to lithium at 980° C.

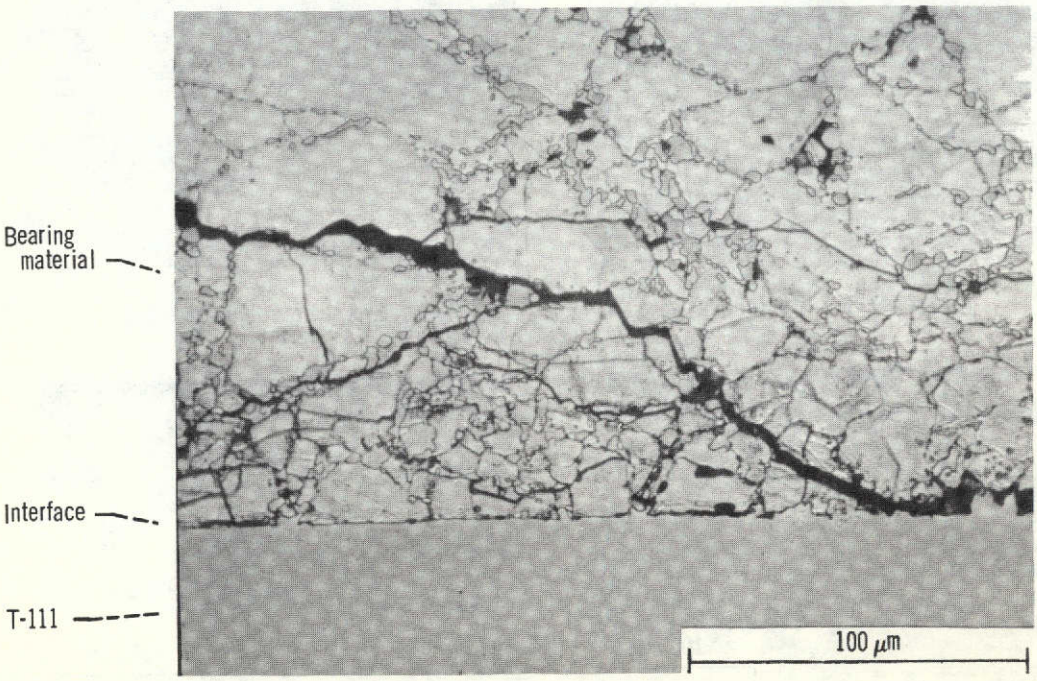


(d) Exposed to lithium at 1090° C.

Figure 9. - Microstructures of surface regions of ZrC-17W specimens before and after exposure to lithium for 4000 hours.

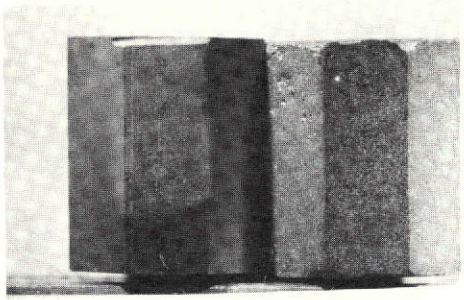


(a) Interface between HfC-2CbC-8Mo and TZM. Etched.

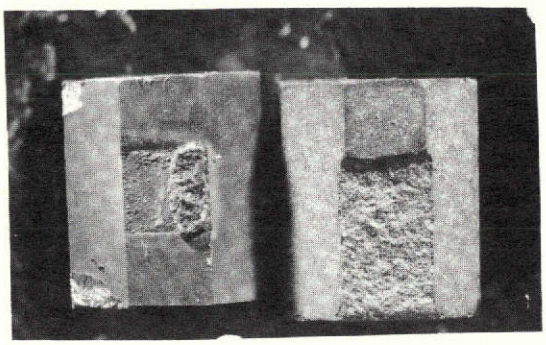


(b) HfN-10W interface between T-111. Etched.

Figure 10. - Bearing materials bonded to refractory alloys after being pressed together at 13.8 meganewtons per square meter (2000 psi) for 1933 hours in lithium at 1200° C.



(a) Tested at 980° C.



(b) Tested at 1200° C.

Figure 11. - Effect of testing temperature on tendency of HfC-2CbC-8Mo to bond to TZM when held together for 1933 hours at $1.4X10^7$ newtons per square meter (2000 psi) in lithium.

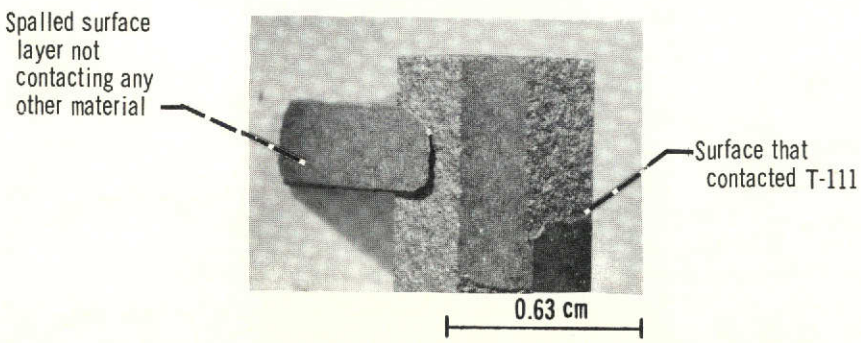
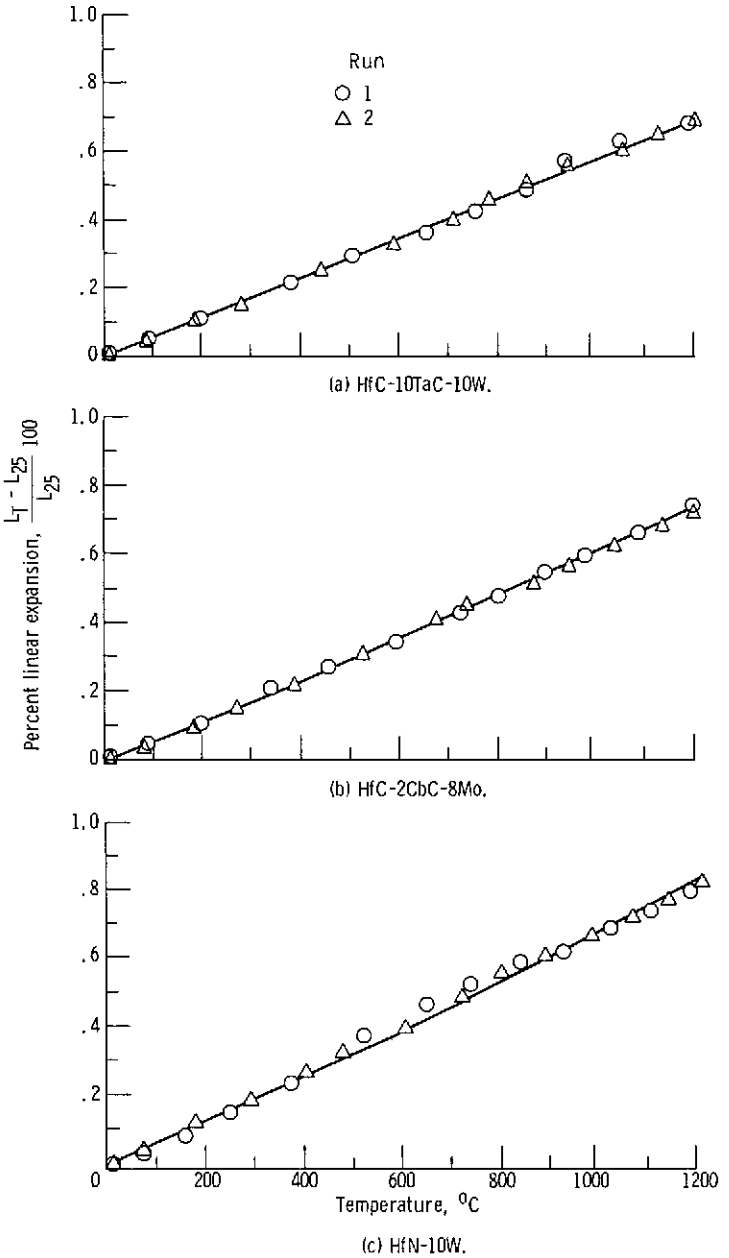


Figure 12. - HfC-2CbC-8Mo bearing specimen after being tested in contact with T-111 at $1.4X10^7$ newtons per square meter (2000 psi) for 1933 hours at 980° C illustrating tendency of material to spall.



(a) HfC-10TaC-10W.

(b) HfC-2CbC-8Mo.

(c) HfN-10W.

Figure 13. - Thermal expansion data for HfC-10TaC-10W, HfC-2CbC-8Mo, and HfN-10W.